5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

The principal route of human exposure to chlorodibromomethane and bromoform is from the consumption of chlorinated drinking water. These chemicals are thought to form in the water as by-products from the reaction of chlorine with dissolved organic matter and bromide ions. Chlorodibromomethane and bromoform concentrations in water are quite variable, but average levels are usually less than 5 μg/L.

Most chlorodibromomethane and bromoform tend to volatilize from water when exposed to the air. The fate of these chemicals in air has not been investigated, but it is likely they are relatively stable, with half-lives of about one to two months. Most measurements of the concentration of these chemicals in air indicate that levels are quite low (less than 10 ppt).

Neither chemical is strongly adsorbed from water by soil materials, and it is likely that both readily migrate in groundwater. Neither chemical appears to be easily biodegradable under aerobic conditions, but they may readily biodegrade under anaerobic conditions. At this time, chlorodibromomethane has been found at 14 of the 1,177 NPL hazardous waste sites in the United States (VIEW Database 1989). The frequency of these sites within the United States can be seen in Figure 5-l. Bromoform has also been found at 14 sites, 13 within the United States (Figure 5-2) and one in the Commonwealth of Puerto Rico.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

No studies were located regarding the amount of bromoform and chlorodibromomethane released into the atmosphere from laboratories, chemical plants, or chemical waste sites. However, since neither compound is produced or used in large quantities (Perwak et al. 1980), atmospheric emissions from these sources are probably small.

5.2.2 Water

The principal source of bromoform and chlorodibromomethane in the environment is chlorination of water containing organic materials (Bellar et al. 1974; EPA 1980a; Rook 1977; Symons et al. 1975). It has been estimated that the total amounts of bromoform and chlorodibromomethane generated by chlorinating United States drinking water in 1978 was 17 and 204 kkg, respectively (Perwak et al. 1980).

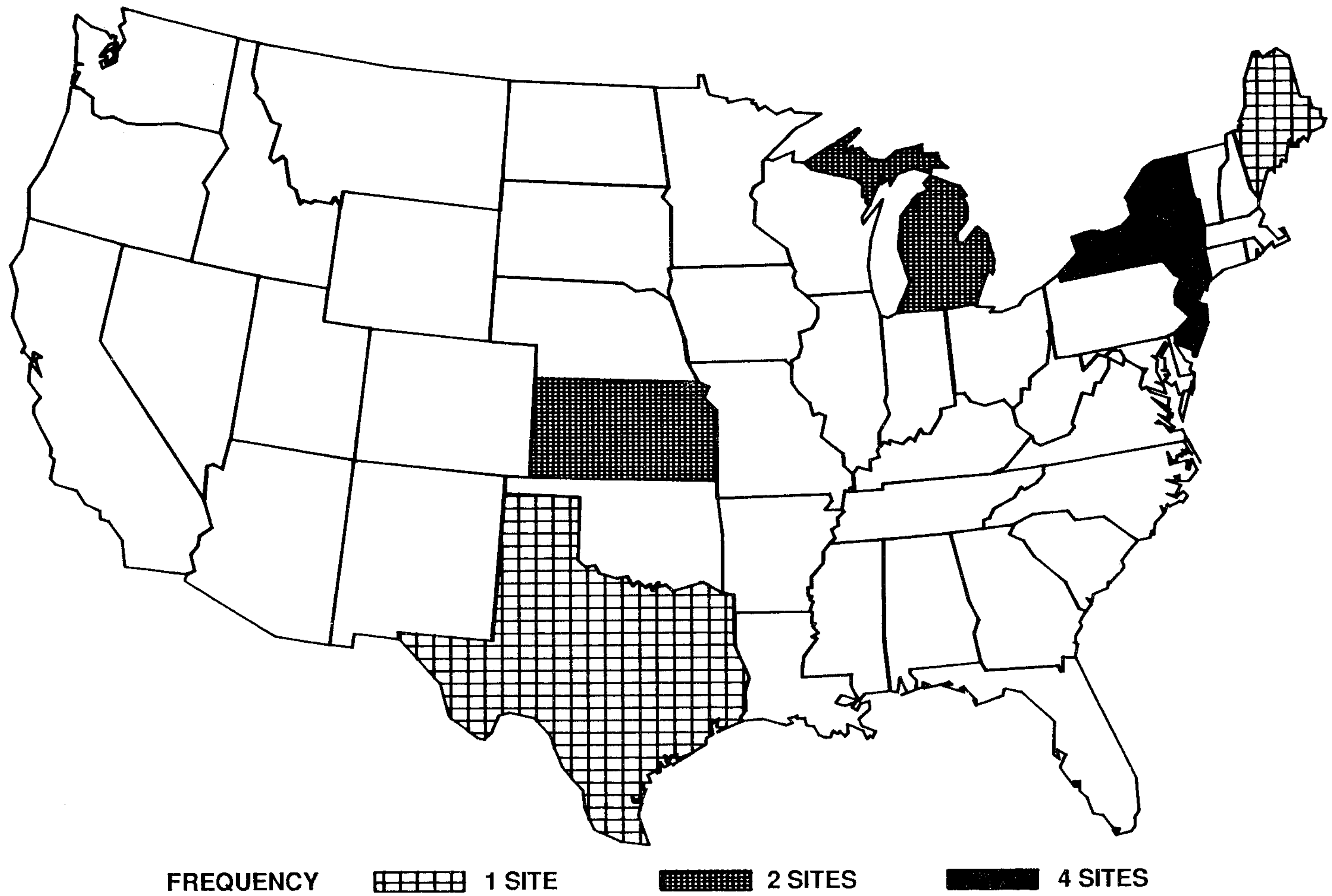

FIGURE 5-1. Frequency of Sites with Chlorodibromomethane Contamination

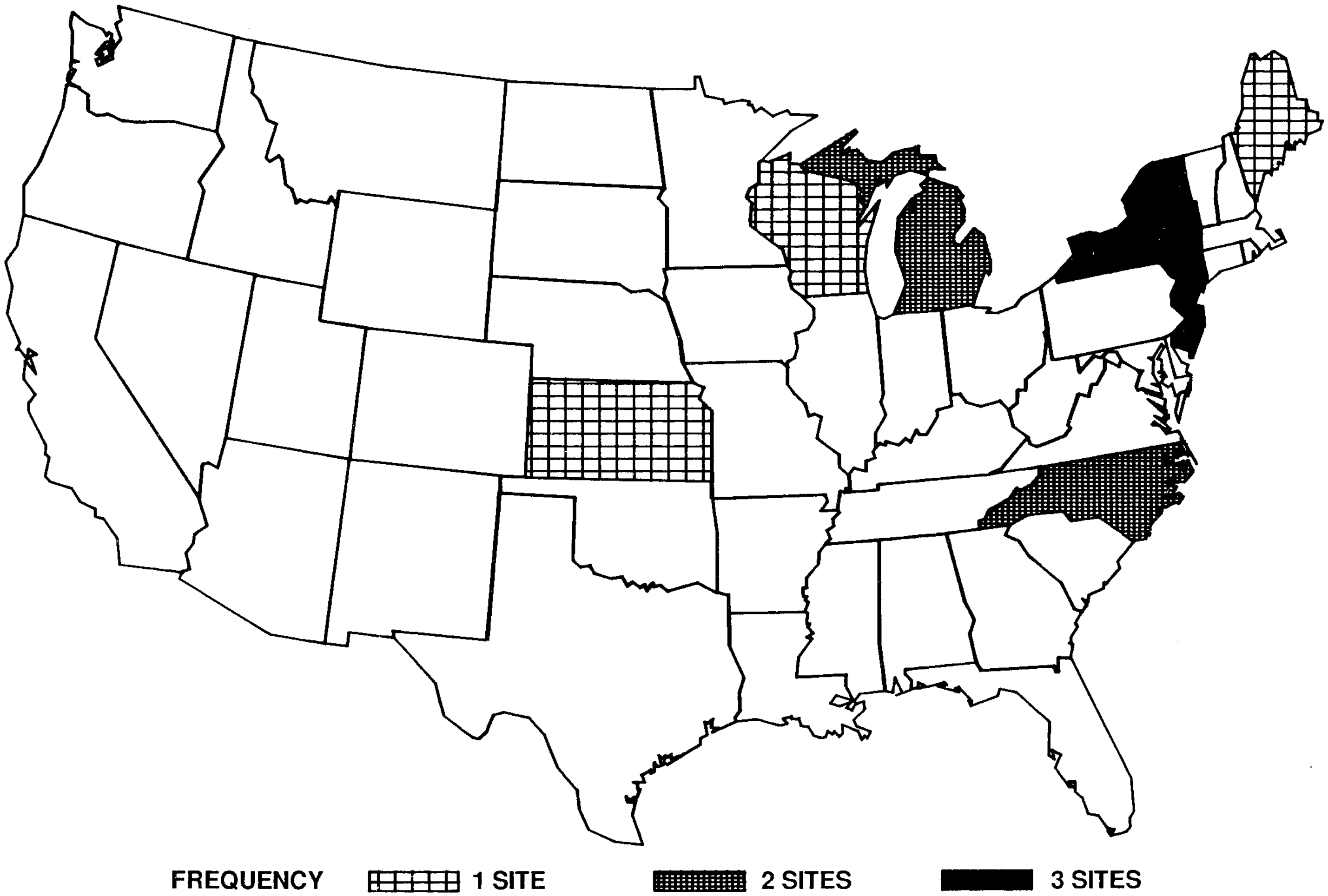

FIGURE 5-2. Frequency of Sites with Bromoform Contamination

Chlorodibromomethane and bromoform may also occur as a consequence of chlorinating industrial waste waters (Perry et al. 1979). Staples et al. (1985) reported that bromoform was detected in 60 of 1,346 samples of industrial waste effluent, at a median concentration of < 5 μg/L, and chlorodibromomethane was detected in 84 of 1,298 samples at a median concentration of < 2.4 μg/L. These values are not significantly higher than those for typical chlorinated water (see Section 5.4.2), suggesting that industrial discharge may not be a major source of release.

Class et al. (1986) observed trace levels of chlorodibromomethane and bromoform and other halogenated methanes in seawater (0.1 to 6 ng/L) and in the air (0.1 to 20 ppt) at several locations in the Atlantic. The presence of these compounds can be attributed to biosynthesis and release of bromochloromethanes by macroalgae (Class et al. 1986; Gschwend et al. 1985). Gschwend et al. (1985) estimated that marine algae could be a major global source of volatile organobromides, but Class et al. (1986) concluded that this source accounts for < 1% of the anthropogenic burden of bromomethanes in the atmosphere.

5.2.3 Soil

Soils and other unconsolidated surficial materials may become contaminated with bromoform and chlorodibromomethane by chemical spills, the landfilling of halomethane-containing solid wastes, or the discharge of chlorinated water. However, no data were located to suggest that land releases are a significant source of the chemicals in the environment.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Bromoform and chlorodibromomethane are slightly volatile liquids, and tend to exist primarily as vapors in the atmosphere. The vapor pressure of bromoform is 0.007 atm at 25°C (Mackay et al. 1982), and the vapor pressure of chlorodibromomethane at 20°C is approximately 0.1 atm (Mabey et al. 1982). The half-time of evaporation from flowing, aerated water (e.g., rivers and streams) has been estimated to range from 1 to 581 hours for bromoform and from 0.7 to 398 hours for chlorodibromomethane (Kaczmar et al. 1984; Mackay et al. 1982).

Both chlorodibromomethane and bromoform are moderately soluble in water (Callahan et al. 1979; Mabey et al. 1982), and so each may be removed from the air by being dissolved into clouds or raindrops. Estimates of the Henry's law constant (H) (the tendency of a chemical to partition between its vapor phase and water) for bromoform range from 4.3 to 5.6 x 10^{-4} atm-m^3/mole, and from 8.7 to 9.9 x 10^{-4} atm-m^3/mole for chlorodibromomethane (Mabey et al. 1982; Mackay and Shiu 1981; Munz and Roberts 1987; Nicholson et al. 1984). The magnitude of these values suggest that the two halomethanes will tend to partition to both water and air.

It is not known if either compound can be adsorbed by airborne particulate matter that is subject to atmospheric dispersion, gravitational settling, or wash-out by rain. Particle adsorption is probably not an important transport mechanism because these chemicals occur at such low concentrations in the atmosphere.

Bromoform and chlorodibromomethane have a minor tendency to be adsorbed by soils and sediments. Calculated and measured values of K_{oc} (the organic carbon/water partition coefficient, an index of the relative mobility of a material in water-soil systems) for bromoform range from 62 to 126 (Hassett et al. 1983; Hutzler et al. 1986; Mabey et al. 1982). These relatively low values imply that bromoform will exhibit only a minor affinity for soil materials and will tend to be highly mobile (Roy and Griffin 1985). This low tendency for adsorption to soil has been confirmed in laboratory studies by Curtis et al. (1986) and in field studies by Roberts et al. (1986).

A similar K_{oc} value of 83 has been estimated for chlorodibromomethane, although this value is uncertain because its solubility in water has not been measured. No studies were located on the adsorption of chlorodibromomethane by soils or soil materials, but it is likely that chlorodibromomethane will have properties generally similar to those of bromoform.

Bromoform and chlorodibromomethane may be slightly bioconcentrated by aquatic organisms. The octanol/water partition coefficient (K_{oc}) (an index of the partitioning of a compound between octanol and water) is approximately 240 for bromoform and 170 for chlorodibromomethane (Mabey et al. 1982). The magnitudes of these values suggest that the chemicals will tend to partition to fat tissues of aquatic organisms. No studies were located regarding the bioconcentration factor for chlorodibromomethane or bromoform, but based on measured BCFs for similar compounds (Kenaga 1980), the bioconcentration factor of chlorodibromomethane and bromoform may be on the order of 2 to 10. It is not known if these chemicals can be transferred through food chains to higher trophic levels, but this seems unlikely to be of major concern.

5.3.2 Transformation and Degradation

5.3.2.l Air

Based on the behavior of similar compounds, it seems likely that bromoform and chlorodibromomethane may be degraded by photooxidative interactions with atmospheric OH radicals. Radding et al. (1977) proposed that the atmospheric half-life of bromoform and chlorodibromomethane is approximately one to two months, but this has not been confirmed by direct experimental measurements.

5.3.2.2 Water

Both chlorodibromomethane and bromoform are relatively stable in water, with estimated hydrolytic rate constants of 3.2×10^{-11} sec^{-1} and 8×10^{-11} sec^{-1} (Mabey and Mill 1978). These rate constants correspond to hydrolytic half-lives of 686 and 274 years for bromoform and chlorodibromomethane, respectively.

No information was located on oxidation or photolysis of these chemicals in water, but it is not expected that either is a significant degradative pathway.

It has been found that chlorodibromomethane and bromoform undergo only limited biodegradation (10 to 25%) under aerobic conditions, although the rate may increase somewhat after microbial adaptation (Bouwer et al. 1981; Tabak et al. 1981a). Under anaerobic conditions, chlorodibromomethane and bromoform have been found to be readily biodegraded in the presence of methane-producing bacteria (Bouwer et al. 1981; Bouwer and McCarty 1983a), and under denitrifying and sulfatereducing conditions in batch and column experiments (Bouwer and McCarty 1983b; Bouwer and Wright 1986). There is also some field evidence that trihalomethanes degrade in anaerobic groundwater (Bouwer et al. 1981), with half-lives estimated to be between 21 and 42 days (Bouwer and McCarty 1984). Bouwer and Wright (1986) reported that one degradation product of bromoform was dibromethane, but there was no additional information on the identity or fate of environmental degradation by-products.

5.3.2.3 Soil

No studies were located regarding the biodegradation of chlorodibromomethane or bromoform in soil, It is expected that observations regarding biodegradation rates in aerobic and anaerobic aqueous media (above) will be generally applicable to degradation rates in moist soils.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Chlorodibromomethane and bromoform are usually found in air only at very low concentrations. Brodinsky and Singh (1983) tabulated data on chlorodibromomethane and bromoform levels in ambient air from five urban locations across the United States. For chlorodibromomethane, 63 of 89 samples were below the detection limit, the mean value was 3.8 ppt (32 ng/m^3), and the highest value was 27 ppt (230 ng/m^3). For bromoform, 60 of 78 samples were below the detection limit, the mean value was 3.6 ppt (37 ng/m^3) and the highest value was 71 ppt (730 ng/m3). The mean concentration of bromoform in ambient air samples collected in the Arctic Circle was 5.1 ppt (53 ng/m^3) (Berg et al. 1984). Forty-six air samples collected near four chemical plants in Arkansas contained a mean bromoform concentration of 0.9 ppt (9 ng/m^3) (Pellizzari 1978). The mean chlorodibromomethane concentration was 0.08 ppt (0.8 ng/m^3), but 54 of 56 measurements were less than 0.05 ppt (0.5 ng/m^3).

No studies were located regarding atmospheric concentrations of bromoform or chlorodibromomethane in the workplace. Chlorodibromomethane was detected in air samples at two hazardous waste sites, but the amounts were not quantified (LaRegina et al. 1986).

5.4.2 Water

Chlorodibromomethane and bromoform are rarely measurable in nonchlorinated water (Cech et al. 1981; Staples et al. 1985; Varma et al. 1984), but both are very frequently found in chlorinated water. The levels of bromoform and chlorodibromomethane in finished (chlorinated) drinking water have been investigated in several studies (see Table 5-l). Except for a few cases, the concentrations of bromoform and chlorodibromomethane in drinking water were less than 100 μg/L, with mean concentrations generally less than 10 μg/L.

It is usually found that halomethanes occur at higher concentrations in drinking water derived from surface sources than those from groundwater supplies because the former tends to contain more dissolved organic matter (Bellar et al. 1974; Cech et al. 1981; Glaze and Rawley 1979; Page 1981). The total trihalomethane content of finished water from a given facility can be extremely variable as a function of time ?Arguello et al. 1979; Smith et al. 1980), with lower levels of halomethanes usually occurring during the winter.

Trihalomethanes may also form in chlorinated swimming pools (Beech et al. 1980). For freshwater pools, chloroform and dichlorobromomethane were usually the predominant THM species present, with chlorodibromomethane and bromoform averaging 3 to 15 and 1 to 2 ,μg/L, respectively. However, in saline pools (which have a higher bromide ion content than freshwater pools), bromoform was the major THM present (average concentration of 650 μ/L), with lower concentrations (5 to 27 μg/L) of chlorodibromomethane, bromodichloromethane, and chloroform.

TABLE 5-1. Occurrence of Bromoform and Chlorodibromomethane in Finished Drinking Water

Frequency of Detection %	Concentration ($\mu g/L$) Range	Mean	Location	Reference
Bromoform				
10	ND-92	≈0.4	national	Symons et al. (1975)
27	ND-3.0	≈0.5	13 cities	Keith et al. (1976)
34	NR	12	national	Brass et al. (1977)
67	NR-4.4	0.4	midwest	ORVWSC (1979)
NR	ND-258	≈7	Texas	Glaze and Rawley (1979)
100	4-17	9	Texas	Smith et al. (1980)
26	NR-110	NR	national	Westrick et al. (1984)
NR	1-10	NR	Iowa	Kelley et al. (1985)
8	ND-1.6	0.1	Michigan	Furlong and D'Itri (1986)
NR	NR	0.8-8	California	Wallace et al. (1986b)
Chlorodibromomethane				
86	<0.1-2	0.9	Ohio	Bellar et al. (1974)
NR	3-32	NR	5 cities	Coleman et al. (1975)
37	ND-110	2.7	national	Symons et al. (1975)
85	ND-15.0	≈0.4	13 cities	Keith et al. (1976)
65	ND-9.0	2.9	Iowa	Morris and Johnson (1976)
86	NR	14	national	Brass et al. (1977)
99	NR-33	5.6	midwest	ORVWSC (1979)
NR	ND-128	≈20	Texas	Glaze and Rawley (1979)
100	11-31	20	Texas	Smith et al. (1980)
42	NR-63	NR	national	Westrick et al. (1984)
NR	1-28	NR	Iowa	Kelley (1985)
75	ND-40	4.1	Michigan	Furlong and D'Itri (1986)
NR	NR	1-2	New Jersey	Wallace et al. (1986a)
NR	NR	8-28	California	Wallace et al. (1986b)

μg = microgram; L = liter; ND = Not detected; NR = Not reported.

Chlorodibromomethane and bromoform have also been detected in water near hazardous waste sites, although this is not common. Data from the Contract Laboratory Program (CLP) Statistical Data Base (CLPSD 1988) indicated that bromoform was detected in surface water at two of 862 hazardous-waste sites; the median concentration was 7 μg/L. Chlorodibromomethane was detected in only one sample (45 μg/L). Bromoform was detected in groundwater samples collected at 4 sites; the median concentration was 26 μg/L.

5.4.3 Soil

Staples et al. (1985) reported that bromoform was not detected in any of 353 sediment samples analyzed. No data were available for chlorodibromomethane. Data from the Contract Laboratory Program Statistic Data Base (CLPSD 1988) indicated chlorodibromomethane and bromoform were detected in soils in only 2 of 862 hazardous waste sites; the median concentrations were 17 μg/kg (bromoform) and 15 μg/kg (chlorodibromomethane).

5.4.4 Other Media

No studies were located regarding the occurrence of bromoform and chlorodibromomethane in food or other media.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Because of the variability of chlorodibromomethane and bromoform concentrations in water and air, it is not possible to derive precise estimates of typical human exposure levels. However, based on the typical ranges of chlorodibromomethane and bromoform concentrations measured in water and air, it is likely that most individuals will be exposed to average doses of less than 1 μg/kg/day (Table 5-2), of which nearly all is due to water. Limited data suggest that exposure levels around chemical factories or waste sites are not likely to be much higher, but this can only be evaluated on a site-by-site basis.

Exposure to chlorodibromomethane and bromoform may be above-average for persons who swim in chlorinated swimming pools. Beech (1980) estimated that the total dose for a six-year old boy who swam for 3 hours in a pool containing 500 μg/L of trihalomethanes could be as high as 2.8 mg (130 μg/kg). About 60% of this dose was attributed to dermal absorption, with about 30% resulting from inhalation. In freshwater pools, only a small fraction of this would be chlorodibromomethane or bromoform, but in a saltwater pool, a large fraction would be expected to be bromoform (Beech et al. 1980).

No studies were located regarding human exposure levels in the workplace.

TABLE 5-2. Summary of Typical Human Exposure to Chlorodibromomethane and Bromoform

Parameter	Exposure Medium	
	Water	Air
Typical concentration in medium	1-20 $\mu g/L$	0-0.1 $\mu g/m^3$
Assumed intake of medium by 70-kg adult	2 L/d	20 m^3/d
Assumed absorption fraction	1.0	0.5
Estimated dose to 70-kg adult	0.03-0.6 $\mu g/kg/d$	0.0-0.01 $\mu g/kg/d$

μg = microgram; L = liter; m^3 = cubic meters; d = day; kg = kilogram.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The environmental medium most likely to be contaminated with bromoform and chlorodibromomethane is chlorinated water. Therefore, any person who is in frequent contact with such water could have above average exposures. This includes individuals who drink large quantities of water, such as workers in hot climates, or individuals with swimming pools or saunas, where contact could occur by inhalation or by dermal contact. Since bromoform and chlorodibromomethane levels in water depend on the organic content of the source water before chlorination, individuals whose water source is high in organics are likely to have finished water with higher-than-average bromoform and chlorodibromomethane levels.

Workers in chemical production facilities or laboratories where bromoform and chlorodibromomethane is made or used would also have potentially high exposures to the chemicals, most likely by inhalation or dermal exposure. Persons living near hazardous-waste sites may have potentially high exposures to bromoform and chlorodibromomethane, but this can only be evaluated on a case-by-case basis.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of chlorodibromomethane and bromoform is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of chlorodibromomethane and bromoform.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. Most of the physical-chemical properties of chlorodibromomethane and bromoform have been measured, but the solubility of chlorodibromomethane in water has only been estimated.

Direct measurement of this value would be valuable in improving estimates of the fate and transport of chlorodibromomethane in aqueous media.

Production, Use, Release and Disposal. Available data indicate that neither bromoform nor chlorodibromomethane is produced or used in significant quantities in the United States. Nevertheless, a listing of laboratories or industries that use small amounts in research or testing would be valuable in identifying locations where the potential for environmental releases or human exposure exists. Also, information on the means of disposal of waste chemicals would be valuable in identifying environmental media likely to be affected at such sites. Federal regulations do restrict disposal of chlorodibromomethane and bromoform to land or in industrial effluents.

According to the Emergency Planning and Community Right to Know Act of 1986 (EPCRTKA), (§3313), (Pub. L. 99-499, Title III, §313), industries are required to submit release information to the EPA. The Toxic Release Inventory (TRI), which contains release information for 1987, became available in May of 1989. This database will be updated yearly and should provide a more reliable estimate of industrial production and emission.

Environmental Fate. The fate of chlorodibromomethane and bromoform in the environment has not been thoroughly studied, although the physical-chemical properties indicate that both are likely to partition to air and water. Volatilization rates have been calculated for flowing rivers and streams, but direct measurements of half-times of volatilization would be useful, both for surface waters and for household water (showers, baths, cooking, etc.). Adsorption of these compounds to soils and sediments has been studied and does not appear to be a significant factor. Consequently, transport in surface or groundwater are likely to be important. Studies to confirm these expectations and provide more precise descriptions of the environmental behavior of these compounds would be valuable in assessing human exposure near specific sources of release.

Degradation of chlorodibromomethane and bromoform in air has not been studied, but is expected to occur by reaction with hydroxyl radicals. Studies to measure the atmospheric half-times of these compounds would be valuable in estimating long-term trends in atmospheric levels, but such studies are probably not essential in estimating exposure near specific sources. Neither chemical undergoes chemical degradation in water, but both are subject to microbial breakdown in water (especially anaerobic groundwater) or moist soils.

Further data on the rate of microbial degradation of chlorodibromomethane and bromoform in water and soil would be valuable, with special attention to how these rates depend on environmental conditions (oxygen level, pH, etc.).

Bioavailability from Environmental Media. Both chlorodibromomethane and bromoform are known to be absorbed following oral and inhalation exposure. No data are available regarding dermal absorption, but it seems likely that uptake across the skin may occur. No data were located regarding the relative bioavailability of chlorodibromomethane and bromoform in water, soil or air. Because of their physical and chemical properties, it is expected that the bioavailability of chlorodibromomethane and bromoform are not significantly reduced by environmental media, but studies to substantiate this presumption would be helpful.

Food Chain Bioaccumulation. There are few data on bioconcentration of chlorodibromomethane or bromoform by plants or aquatic organisms, and no data were located on the bioaccumulation of bromoform and chlorodibromomethane in the food chain. This lack of data may not be a major limitation because the general levels of the chemicals in water and soil appear to be quite low, and based on the K_{oc} of these chemicals, there appears to be a low likelihood of food chain buildup.

Exposure Levels in Environment Media. There are several studies on the atmospheric concentrations of bromoform and chlorodibromomethane in urban and rural environments, but many of the samples did not have detectable levels. No data on levels in air near waste sites were located. More research in this area using more sensitive analytical methods would be helpful, although it is anticipated that typical atmospheric levels will usually be low enough that air is not the principal route of exposure. Data are available on chlorodibromomethane and bromoform in a number of chlorinated drinking water systems, and these compounds have been detected in surface water and groundwater near a few hazardous waste sites. Further studies on the levels of these compounds in water and soil around waste sites would be valuable in evaluating the risk to human health posed by these contaminants.

Exposure Levels in Humans. There are no data on levels of chlorodibromomethane or bromoform in blood, breath or other tissues from humans residing near waste sites. Low levels of bromoform have been detected in blood of humans, presumably as the result of exposure through ingestion of chlorinated drinking water. Levels in expired breath and in adipose tissue appear to be too low to measure reliably for the general population. Direct measurement of typical human intake from water and air (especially indoor air) would be helpful in obtaining more accurate estimates of typical human dose levels. Similar data on inhalation and dermal doses would be useful for bromoform and chlorodibromomethane in and around swimming pools (especially indoor pools).

Exposure Registries. No exposure registries for bromoform and chlorodibromomethane were located. These compounds are not currently among the compounds for which subregistries have been established in the National Exposure Registry. These compounds will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to these compounds.

5.7.2 On-going Studies

No information was located on any on-going studies on the fate and transport of bromoform and chlorodibromomethane, or on the potential for human exposures to these chemicals.

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, will be analyzing human blood samples for chlorodibromomethane, bromoform, and other volatile organic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.